589. *The Thermal Unimolecular Isomerization of* 1,1,2,2-*Tetramethylcyclopropane.*

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The thermal isomerization of 1,1,2,2-tetramethylcyclopropane has been investigated between 435 and 484°c. In this range, in an " aged " reaction vessel, the isomerization is homogeneous and of first order. Available evidence indicates that the isomerization is a true unimolecular transformation; the primary product is 2,4-dimethylpent-2-ene. The first-order rate constant begins to decrease at a pressure of about 0·5 mm. The " high-pressure " rate constants fit the Arrhenius equation

$$k = 10^{15\cdot83} \exp(-64{,}400/\boldsymbol{R}T) \text{ sec.}^{-1}.$$

Some isomerization and decomposition of the 2,4-dimethylpent-2-ene occurs during the cyclopropane rearrangement but at a considerably slower rate than that of the primary reaction.

Among the best authenticated unimolecular reactions are the thermal isomerizations of cyclopropane[1] and some alkylcyclopropanes.[2] These reactions are all homogeneous, first-order, non-chain processes. Further, the predicted " fall off " of the first-order rate constant at low pressures has been observed for all these compounds. The present work describes experiments with the most highly substituted cyclopropane yet investigated in detail.

Experimental

The 1,1,2,2-tetramethylcyclopropane (American Petroleum Institute Standard Sample) was stated to have a purity of 99·96 ± 0·03%. It was degassed before use but no further attempt at purification was made.

2,4-*Dimethylpent*-2-*ene*.—Di-isopropyl ketone was reduced to 2,4-dimethylpentan-3-ol by the Meerwein–Pondorff–Verley reaction.[3] This alcohol was treated with concentrated sulphuric acid to yield 2,4-dimethylpent-2-ene. The crude olefin was distilled under reduced pressure at 0° to give 2,4-dimethylpent-2-ene of 95% purity (the other 5% consisting of various seven-carbon olefins). An alternative dehydration of the xanthate formed from 2,4-dimethylpentan-3-ol also yielded 2,4-dimethylpent-2-ene of about 95% purity.

Apparatus.—A conventional " static " high-vacuum apparatus was used. That part of the apparatus consisting of reaction vessel, sample container, and gas pipette, through which the reactant and products flowed, was isolated from the remainder of the vacuum system by diaphragm valves. This ensured that errors due to absorption of these vapours in stopcock

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[1] Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.

[2] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; Flowers and Frey, *J.*, 1959, 3953; Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 121; 1961, *A*, **260**, 424.

[3] Vogel, " Text-book of Practical Organic Chemistry," 3rd edn., Longmans, Green & Co., London 1956, p. 883.

grease were avoided. By mounting a diaphragm valve to the capillary inlet of the reaction vessels, close to the furnace, it was possible to reduce the deadspace to 0·2%. Most isomerizations were carried out in a cylindrical Pyrex vessel (volume 160 ml.) fitted with a thermocouple well. In a few runs a vessel packed with glass tubes was used. The furnace was tapped at 3 points for external shunts and could be operated with a temperature gradient of only 0·3°c over the entire vessel. The furnace was supplied from a constant voltage transformer and controlled by a Sunvic R.T.2 regulator and could be maintained indefinitely to within 0·1°c. The temperature was measured by using a platinum/platinum–rhodium thermocouple which had been calibrated against a standard platinum resistance thermometer.

Procedure.—1,1,2,2-Tetramethylcyclopropane was admitted to the reaction vessel from a gas pipette. After each run the entire contents of the vessel were frozen into a previously evacuated sample bulb (about 100 ml.), cooled in liquid oxygen. Between runs the vessel was pumped down to better than 10^{-4} mm. Initially the vessel was " aged " by carrying out runs until reproducible rate constants were obtained.

Analysis.—Reaction mixtures were analysed by gas chromatography in a specially designed apparatus. This consisted of a gas-sampling system employing a Toepler pump, a 30 ft. × 0·17 in. (internal diam.) coiled copper column packed with 40—60 mesh Chromosorb containing 20% w/w of di-2-cyanoethyl ether and maintained at 33°c. Hydrogen was used as the carrier gas, and a Gow–Mac tungsten filament katharometer as detector. Signals from the detector (in a conventional Wheatstone bridge network) were fed *via* a variable attenuator to a Sunvic RSP 2 0—1 mv recorder fitted with a retransmitting slidewire. This slidewire (fed by 5 accumulators) was used to drive a low-inertia integrating motor (Electro-Methods) coupled to a revolution counter. For some runs the katharometer signals were integrated by using a Speedomax Type G recorder connected to a Perkin–Elmer model 194 integrator. From the integrated area of the chromatographic peaks an analytical precision better than 0·5% was obtained. All stopcocks on the gas-inlet system of the analytical apparatus were lubricated with a special fluorocarbon grease to minimize absorption errors.

Products were identified initially by retention times on the gas-chromatography column. More positive identification was obtained by trapping out chromatographic peaks followed by infrared and mass spectrometric analysis.

RESULTS AND DISCUSSION

In the temperature range 435—484°c 1,1,2,2-tetramethylcyclopropane undergoes a first-order isomerization to 2,4-dimethylpent-2-ene:

Preliminary runs at 452°c with various pressures of the tetramethylcyclopropane showed that the rate constant for the isomerization was independent of pressure from 22·5 to 2·0 mm. Detailed studies were, therefore, undertaken at 5 mm. pressure at 6 temperatures. At each temperature at least 7 runs were carried out in which the decomposition varied from 5 to 50%. At the higher-percentage decompositions (and especially at the higher temperatures) some cracking products were formed. As a result, plots of the logarithm of the percentage of undecomposed cyclopropane against time were only linear up to about 35% decomposition. If, however, allowance was made for the formation of these cracking products (this will be referred to later) linear plots could be obtained including the results obtained at higher percentage conversions.

The first-order rate constants obtained are shown in the Table.

Rate constants for the isomerization of 1,1,2,2-tetramethylcyclopropane.

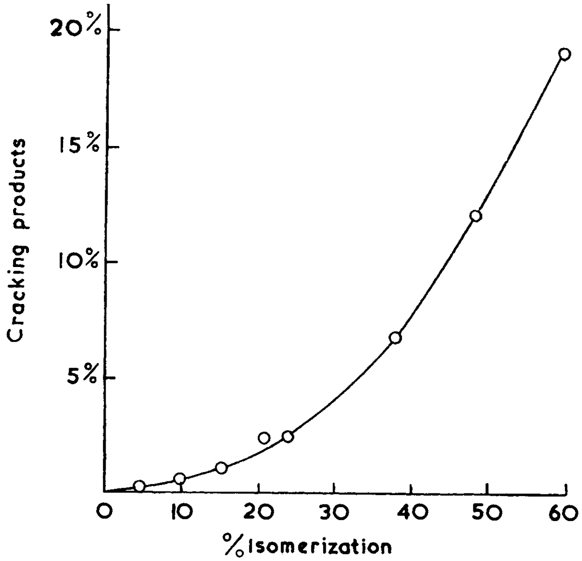
Temp. (°c)	434·8	440·9	452·0	462·4	473·0	483·6
10^5k (sec.$^{-1}$)........................	3·81	5·62	11·8	20·4	39·2	75·9

An Arrhenius plot of these results gave a good straight line. The frequency factor and energy of activation were calculated by the method of least squares, giving $k = 10^{15\cdot83}$

$\exp(-64{\cdot}400/RT)$ sec.$^{-1}$. The estimated maximum error in the energy of activation is $\pm 1{\cdot}5$ kcal./mole.

All the rate data refer to the " aged " reaction vessel. To ensure that these rate constants were for the homogeneous reaction, a series of runs were carried out in a packed vessel at 472°c which had a surface to volume ratio 5·8 times greater than the unpacked vessel. After correction for the 1° change in temperature the same rate was obtained as in the unpacked vessel at 473°c. No attempt was made to rule out a radical-chain component of the reaction by the addition of such inhibitors as nitric oxide or propene, since the product of the reaction, 2,4-dimethylpent-2-ene, will itself be a powerful inhibitor. Since no curvature of the first-order plots was observed at low-percentage decomposition it seems clear that no such component occurs to any appreciable extent.

As has been mentioned, at high-percentage conversions appreciable quantities of cracking products, *i.e.*, molecules containing less than seven carbon atoms, were formed. A plot of the percentage of cracking products against the percentage isomerization is shown in the Figure. These values were obtained by assuming that the sum of the integrated peak areas of the various products was proportional to their mole percentage. This is certainly no better than a crude approximation but this does not affect the general shape of the curve shown.



Yield of cracking products as a function of percentage isomerization.

As will be seen, the plot shows positive curvature and has zero slope at zero decomposition. This implies that the cracking products are all secondary and arise from the 2,4-dimethylpent-2-ene. Since at least 2 molecules of such products must arise from each molecule of the olefin which decomposes the effect on the measured rate constant due to the cracking reaction is a good deal less than might be supposed from a casual inspection of the Figure.

In addition to the cracking reactions, 2,4-dimethylpent-2-ene also undergoes isomerizations to give other seven-carbon olefins. These reactions are considerably slower than the primary reaction being investigated. However, at high-percentage conversions a definite shoulder appeared on the chromatographic peak due to 2,4-dimethylpent-2-ene. By trapping the tail of this chromatographic peak (it was necessary to combine the fractions obtained from a number of runs) it was possible to obtain a large enough sample to carry out a mass-spectrometric analysis and also an infrared spectral analysis in a gas microcell. The mass spectrum indicated a compound of formula C_7H_{14}.

However, no single seven-carbon olefin whose mass spectrum was available had a similar cracking pattern. It was concluded that at least two isomeric olefins were present. The infrared spectrum indicated the presence of two olefins with terminal double bonds, but the possibility of a third olefin without a terminal double bond cannot be excluded. Since the main purpose was not concerned with this secondary isomerization, no further attempts were made at more complete identification of these products.

Provided a sufficiently low pressure is reached, the rate constant of a unimolecular reaction must start to decrease with decreasing pressure. For cyclopropane this fall off has already started at 1000 mm. and for methylcyclopropane fall off starts at about 100 mm. Dimethylcyclopropane starts to show fall off at about 16 mm., so it is quite clear that these results confirm the theoretical expectation that for a series of unimolecular reactions having similar values for their Arrhenius parameters the pressure at which fall off commences will decrease as the molecular complexity increases. Accordingly, for 1,1,2,2-tetramethylcyclopropane fall off is expected to commence at pressures appreciably lower than 10 mm. To test this point, a series of runs was carried out at pressures below 5 mm. The design of the apparatus prevented pressures below 0·2 mm. being employed, and further the occurrence of the cracking reactions already referred to prevented results of high precision being obtained. However, in the range investigated fall off became apparent at approximately 0·5 mm.

The isomerizations of cyclopropane and alkylcyclopropanes are all characterized by very large A factors. The A factor of $10^{15 \cdot 83}$ obtained in this work is the highest of the series. This is remarkable especially when it is realized that in the case of cyclopropane ($A = 10^{15 \cdot 2}$) there is a degeneracy of 12 in the reaction path whereas in the tetramethyl compound this degeneracy is reduced to 4. It is possible that the observed energy of activation is somewhat high, though allowing even the maximum probable error only reduces the value to $10^{15 \cdot 4}$. This high value does suggest an even " looser " transition state than occurs in the related isomerizations. The experimental evidence at present available is, however, not strong enough to warrant the development of this idea more fully.

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